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Article

Heterometallic Compounds Assembled from Ferrocene-Containing Bisthiosemicarbazone Clips

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Heteropolynuclear organometallic compounds have been constructed by using the ferrocene-based ligand H_2L, $[NH_2SCNHN=C(CH_3)(C_5H_4)]_2Fe$. Reaction of the ligand H_2L with the cobalt(II) salt gave a tetranuclear helicate Co_2Fe_2 (**1**) with two ferrocene-based clips wrapped around the two cobalt atoms. The chiral helicates recognized the neighbors with same chirality through intermolecular hydrogen bonding between the thiosemicarbazone moieties to form a one-dimensional chiral channel. Reaction of the ligand H_2L with the cadmium(II) salt afforded a tetranuclear dimeric compound Cd_2Fe_2 (**2**), with two symmetric related parts bridged through two sulfur atoms. Reaction of the ligand H_2L with the copper(I) salt, in the presence of triethylamine, resulted in a hexanuclear compound Cu_4Fe_2 (**3**) with a crownlike Cu_4S_4 octagon similar to that of S_8 sited inside and two ferrocene-containing ligands positioned outside. Electrochemical measurements were displayed to investigate the redox communications between the ferrocene moieties through metal centers.

Introduction

It is well-established that self-assembly provides direct access to the spontaneous and selective formation of organized supramolecular architectures comprising spatially and geometrically well-defined arrays of metal ions.[1−3] The structure of the bridging group, the metal binding moiety, the metal coordination geometry as well as noncovalent interactions all indicate the architecture obtained. The application of metal−ligand interactions has proved particularly fruitful, and a considerable variety of frequently predesigned molecular architectures[3,4] with unusual and interesting properties[5,6] has been assembled. To design species presenting specific structural and functional features, it is of great importance to establish the rules by which control of the self-assembly process can be achieved through chemical programming by means of suitable components and assembling algorithms.

Thiosemicarbazones and their metal complexes have been attracting considerable interest due to their biological activities, such as antiviral, antibacterial, antimalarial, antifungal,

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(1) (a) Lehn, J. M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH: Weinheim, Germany, 1995. (b) *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Lehn, J. M., Eds.; Pergamon: Oxford, U.K., 1996; Vol. 9, pp 165−211.
(2) (a) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (b) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483. (c) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (d) Schwab, P. F. H.; Levin, M. D.; Michl, J. *Chem. Rev.* **1999**, *99*, 1863. (e) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375. (f) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417. (g) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638.
(3) (a) Schnebeck, R. D.; Freisinger, E.; Glahe, F.; Lippert, B. *J. Am. Chem. Soc.* **2000**, *122*, 1381. (b) Sun, S. S.; Lees, A. J. *J. Am. Chem. Soc.* **2000**, *122*, 8956. (c) Biradha, K.; Aoyagi, M.; Fujita, M. *J. Am. Chem. Soc.* **2000**, *122*, 2397. (d) Yu, S. Y.; Kusukawa, T.; Biradha, K.; Fujita, M. *J. Am. Chem. Soc.* **2000**, *122*, 2665. (e) Sautter, A.; Schmid, D. G.; Jung, G.; Würthner, F. *J. Am. Chem. Soc.* **2001**, *123*, 5424.

(4) (a) Mamula, O.; von Zelewsky, A.; Bernardinelli, G. *Angew. Chem., Int. Ed.* **1998**, *37*, 290. (b) Fujita, M.; Fujita, N.; Ogura, K.; Yamaguchi, K. *Nature* **1999**, *400*, 52. (c) Olenyuk, B.; Whiteford, J. A.; Fechtenkötter, A.; Stang, P. J. *Nature* **1999**, *398*, 796. (d) Campos-Fernander, C. S.; Clerac, R.; Dunbar, K. R. *Angew. Chem., Int. Ed.* **1999**, *38*, 3477.
(5) (a) Würthner, F.; Sautter, A. *Chem. Commun.* **2000**, 445. (b) Würthner, F.; Sautter, A.; Schmid, D.; Weber, P. J. A. *Chem.−Eur. J.* **2001**, *7*, 894. (c) Benkstein, K. D.; Hupp, J. T.; Stern, C. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 2891. (d) Hartmann, H.; Berger, S.; Winter, R.; Fiedler, J.; Kaim, W. *Inorg. Chem.* **2000**, *39*, 4977.
(6) (a) Slone, R. V.; Benkstein, K. D.; Belanger, S.; Hupp, J. T.; Guzei, I. A.; Rheingold, A. L. *Coord. Chem. Rev.* **1998**, *171*, 221. (b) Lengo, E.; Milani, B.; Zangrando, E.; Geremia, S.; Alessio, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 1096. (c) Guo, D.; Duan, C. Y.; Lu, F.; Hasegawa, Y.; Meng, Q. J.; Yanagida, S. *Chem. Commun.* **2004**, 1486.

and antitumoral activities[7,8] and nonlinear optical properties.[9] Importantly, thiosemicarbazones are versatile ligands that can coordinate as neutral ligands or in the deprotonated form and are flexible spacers with potential multiple binding sites that can be used to construct coordination polymers with multiple dimensions and various topologies.[10,11] The hydrogen atoms attached to the amino nitrogen atoms of the thiosemicarbazone moiety also have the ability to form donor hydrogen bonds from which small, simple fragments can be assembled into the desired cavities under favorable conditions, which is important in host−guest chemistry and has applications in chemistry, biology, and materials science.[11e,12]

On the other hand, from the viewpoint of constructing functional supramolecular compounds, it may be interesting to incorporate functional groups into the ligand instead of the nonfunctional spacers.[13] Organometallic compounds, especially ferrocene and its derivatives, have been pursued with the objective of generating materials possessing useful electrochemical, magnetic, optical, and nonlinear optical properties.[14,15] It is suggested that introducing a ferrocene group into coordination supramolecular systems not only incorporates a redox-active group but also leads to interesting assembled structures, because of the conformational flex-
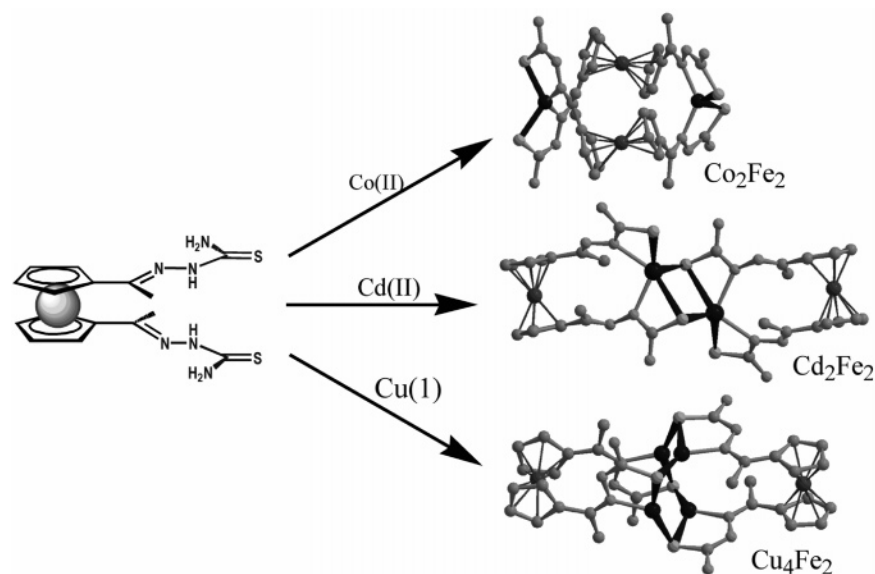
ibility of the ferrocene moieties and the various coordination numbers of metal ions.[16,17] As continuance of our research works in the preparations and properties of ferrocene−metal complexes,[18] here we reported new heterodimetallic compounds derived from a ferrocene-containing bisthiosemicarbazone ligand H_2L, $[NH_2SCNHN=C(CH_3)(C_5H_4)]_2Fe$. It is expected that the conformational freedom of ferrocene and the hydrogen bonds derived from the amino nitrogen atoms of the thiosemicarbazone afford opportunities for generating novel topologies (Scheme 1).

Experimental Section

General Procedures. The ligand H_2L, $[NH_2SCNHN=C(CH_3)(C_5H_4)]_2Fe$, was prepared by the literature method.[11e] All other chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Reactions were carried out in air unless noted otherwise. The elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240 analyzer. The infrared spectra were recorded on a Vector 22 Bruker spectrophotometer with KBr pellets in the 4000−400 cm^{-1} regions. Differential pulse voltammetry results were recorded with an EG&G PAR model 273 instrument. The solution-state measurement were performed in DMF with n-Bu$_4$NClO$_4$ (0.1 mol·dm^{-3}) as supporting electrolyte, in a three-electrode cell that has a 50 ms pulse width with current samples 40 ms after the pulse was applied. The cell comprises a platinum wire working electrode, a platinum auxiliary electrode, and SCE as reference electrode.

Co$_2$Fe$_2$ (1). Co(CH$_3$COO)$_2$·4H$_2$O(0.25 g,1 mmol) suspended in methanol (60 mL) was added dropwise at room temperature to a mixture of H_2L (0.42 g, 1 mmol) and KOH (0.12 g, 2 mmol) in 15 mL of absolute methanol. Amorphous orange solids separated out immediately. After refluxing for 4 h with stirring, a dark-red precipitate was filtered, washed with methanol, and dried in vacuo over P$_2$O$_5$. The crystals suitable for X-ray structure analysis were prepared by slowly diffusing a layer of CH$_3$CN into a layer of DMF solution containing complex **1** in a test tube. Yield: 75%. Anal. Calcd (%) for (C$_{16}$H$_{18}$N$_6$S$_2$FeCo)$_2$·CH$_3$CN·0.5H$_2$O: C, 41.0; H, 4.1; N, 18.3. Found: C, 40.6; H, 4.0; N, 18.2. IR (KBr, cm^{-1}): 3442,

(7) (a) Moham, M.; Agarawal A.; Jha, N. K. *J. Inorg. Biochem.* **1988**, *34*, 41. (b) Easmon, J.; Pürstinger, G.; Heinisch, G.; Roth, T.; Fiebig, H. H.; Holzer, W.; Jäger, W.; Jenny M.; Hofmann, J. *J. Med. Chem.* **2001**, *44*, 2164. (c) Cowley, A. R.; Dilworth, J. R.; Donnelly P. S.; Labisbal, S. A. *J. Am. Chem. Soc.* **2002**, *124*, 5270.

(8) West, D. X.; Liberta, A. E.; Padhye, S. B.; Chikate, R. C.; Sonawane, P. B.; Kumbhar A. S.; Yerande, R. G. *Coord. Chem. Rev.* **1993**, *123*, 49. (b) Lima, G. M.; Neto, J. L.; Beraldo, H.; Siebald, H. G. L.; Duncalf, D. J. *J. Mol. Struct.* **2002**, *604*, 287. (c) Casas, J. S.; Garcýa-Tasend K. S.; Sordo, J. *Coord. Chem. Rev.* **2000**, *209*, 431.

(9) (a) Tian, Y. P.; Duan, C. Y.; Zhao, C. Y.; You, X. Z.; Mak T. C. W.; Zhang, Z. Y. *Inorg. Chem.* **1997**, *36*, 1247. (b) Liu Z. H.; Duan C. Y.; Hu, J.; You, X. Z. *Inorg. Chem.* **1999**, *38*, 1719. (c) Liu, Z. H.; Duan, C. Y.; Li, J. H.; Liu, Y. J.; Mei, Y. H.; You, X. Z. *New J. Chem.* **2000**, *24*, 1057.

(10) (a) López-Torres, E.; Mendiola, M. A.; Pastor C. J.; Pérez, B. S. *Inorg. Chem.* **2004**, *43*, 5222. (b) Ashfield, L. J.; Cowley, A. R.; Dilworth J. R.; Donnelly P. S. *Inorg. Chem.* **2004**, *43*, 4121. (b) Quiroga A. G.; Ranninger, C. N. *Coord. Chem. Rev.* **2004**, *248*, 119. (d) Santos, I. G.; Abram, U.; Alberto, R.; Lopez E. V.; Sanchez, A. *Inorg. Chem.* **2004**, *43*, 1834.

(11) (a) Pal, I.; Basuli, F.; Mak. T. C. W.; Bhattacharya, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 2923. (b) Duan, C. Y.; Liu, Z. H.; You, X. Z.; Xue F.; Mak, T. C. W. *Chem. Commun.* **1997**, 381. (c) He, C.; Duan, C. Y.; Fang, C. J.; Liu Y. J.; Meng, Q. J. *J. Chem. Soc., Dalton Trans.* **2000**, 1207. (d) Han, G.; Guo, D.; Duan, C. Y.; Mo, H.; Meng Q. J. *New. J. Chem.* **2002**, *26*, 1371. (e) Fang, C. J.; Duan, C. Y.; He C.; Meng, Q. J. *Chem. Commun.* **2000**, 1187.

(12) (a) Mendoza, J. De. *Chem. Eur. J.* **1998**, *4*, 1373. (b) Rebek, J., Jr. *Acc. Chem. Res.* **1999**, *32*, 278. (c) MacGillivray L. R.; Atwood, J. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 1018. (d) Fang, C. J.; Duan, C. Y.; He, C.; Han, G.; Meng, Q. J. *New J. Chem.* **2000**, *24*, 69.

(13) (a) Fujita, N.; Biradha, K.; Fujita, M.; Sakamoto, S.; Yamaguchi, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 1718. (b) Abrahams, B. F.; Hoskins, B. F.; Michail, D. M.; Robson, R. *Nature* **1994**, *369*, 727. (c) Lin, K. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2730. (d) Sharma, C. V. K.; Broker, G. A.; Huddleston, J. G.; Baldwin, J. W.; Metzger, R. M.; Rogers, R. D. *J. Am. Chem. Soc.* **1999**, *121*, 1137.

(14) (a) Plenio, H.; Aberle, C.; Al Shihadeh, Y.; Lloris, J. M.; Martinez-Manez, R.; Pardo, T.; Soto, J. *Chem. Eur. J.* **2001**, *7*, 2848. (b) Jutzi, P.; Lenze, N.; Neumann, B.; Stammler, H. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 1424. (c) *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*; Togni, A., Hayashi, T. Eds. VCH: Weinheim, Germany, **1995**. (d) Long, N. J. *Metallocenes: An Introduction to Sandwich Complexes*; Blackwell Science, Inc.: Cambridge, MA, 1998. (e) Bradley, S.; Camm, K. D.; Liu, X. M.; McGowan, P. C.; Mumtaz, R.; Oughton, K. A.; Podesta, T. J. Thornton-Pett, M. *Inorg. Chem.* **2002**, *41*, 715.

(15) (a) Li, G.; Hou, H. W.; Li, Z. F.; Meng, X. R.; Fan, Y. T. *New. J. Chem.* **2004**, *28*, 1595. (a) Li, G.; Hou, H. W.; Li, L. K.; Meng, X. R.; Fan, Y. T.; Zhu, Y. *Inorg. Chem.* **2003**, *42*, 4995. (c) Hou, H. W.; Li, L. K.; Li, G.; Fan, Y. T.; Zhu, Y. *Inorg. Chem.* **2003**, *42*, 3501. (d) Li, G.; Song, Y. L.; Hou, H. W.; Li, L. K.; Fan, Y. T.; Zhu, Y.; Meng, X. R.; Mi, L. W. *Inorg. Chem.* **2003**, *42*, 913.

(16) (a) Braga, D.; Maini, L.; Grepioni, F. *J. Organomet. Chem.* **2000**, *594*, 101. (b) Crespo, O.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Sarroca, C. *Chem. Commun.* **1998**, 1481. (c) Crespo, O.; Canales, F.; Gimeno, M. C.; Jones, P. G.; Laguna, A. *Organometallics.* **1999**, *18*, 3142. (d) Grosche, M.; Herdtweck, E.; Peters, F.; Wagner, M. *Organometallics.* **1999**, *18*, 4669. (e) Maricic, S.; Berg, U.; Frejd, T. *Tetrahedron.* **2002**, *58*, 3085.

(17) (a) Shum, S. P.; Pastor, S. D.; Rihs, G. *Inorg. Chem.* **2002**, *41*, 127. (b) Mata, J. A.; Peris, E. *J. Chem. Soc., Dalton Trans.* **2001**, 3634. (c) Moriuchi, T.; Yoshida, K.; Hirao, T. *Organometallics* **2001**, *20*, 3101. (d) Moriuchi, T.; Nomoto, A.; Yoshida, K.; Ogawa, A.; Hirao, T. *J. Am. Chem. Soc.* **2001**, *123*, 68. (e) Braga, D.; Polito, M.; Bracaccini, M.; D'Addario, D.; Tagliavini, E.; Proserpio, D. M.; Grepioni, F. *Chem. Commun.* **2002**, 1080.

(18) (a) Fang, C. J.; Duan, C. Y.; Mo, H.; He, C.; Meng, Q. J.; Liu, Y. J.; Mei, Y. H.; Wang, Z. M. *Organometallics.* **2001**, *20*, 2525. (b) Fang, C. J.; Duan, C. Y.; Guo, D.; He, C.; Meng, Q. J.; Wang, Z. M.; Yan, C. H. *Chem. Commun.* **2001**, 2540. (c) Guo, D.; Han, G.; Duan, C. Y.; Pang, K. L.; Meng, Q. J. *Chem. Commun.* **2002**, 1096. (d) Guo, D.; Mo, H.; Duan, C. Y.; Lu, F.; Meng, Q. J. *J. Chem. Soc., Dalton Trans.* **2002**, 2593. (e) Guo, D.; Li, Y. T. Duan, C. Y.; Mo, H.; Meng, Q. J. *Inorg. Chem.* **2003**, *42*, 2519. (f) Guo, D.; Zhang, B. G.; Duan, C. Y.; Cao, X.; Meng, Q. J. *J. Chem. Soc., Dalton Trans.* **2003**, 282.

Scheme 1. Various Molecular Structures Derived from the Clips with Different Metal Centers

Table 1. Crystal Date and Structure Refinements for Complexes 1−3

	1	2	3
formula	$C_{34}H_{41}Co_2Fe_2N_{13}O_{0.5}S_4$	$C_{22}H_{32}CdFeN_8O_2S_2$	$C_{71.5}H_{92}Cu_8Fe_4N_{26}O_{3.5}S_8$
formula weight	996.59	672.93	2359.91
T/K	293(2)	293(2)	293(2)
crystal system	monoclinic	triclinic	monoclinic
space group	$C2/c$	$P\bar{1}$	$P2_1$
a/Å	29.031(9)	9.132(3)	17.146(17)
b/Å	9.611(3)	11.341(4)	33.15(3)
c/Å	21.122(7)	15.147(5)	17.399(17)
α/deg		68.733(6)	
β/deg	131.954(6)	86.907(7)	95.82(2)
γ/deg		71.148(7)	
V/Å^3	4383(2)	1379.9(8)	9837(17)
Z	4	2	4
$F(000)$	2036	684	4780
ρ_{calcd}/g cm^{-1}	1.524	1.620	1.585
μ/mm^{-1}	1.628	1.483	2.487
Flack parameter			0.19(2)
R_{int}	0.0735	0.0751	0.0667
wR$_2$	0.1424	0.1497	0.151
GOOF	1.031	1.046	1.041

3288 (ν_{N-H}, ν_{O-H}, m), 1658 ($\nu_{C=N}$, s), 1493 (ν_{C-N}, s), 1296 (ν_{N-N}, m), 1041 ($\nu_{C=S}$, m).

Cd$_2$Fe$_2$ (2). The complex **2** was prepared in a procedure similar to that of **1**, except using Cd(CH$_3$COO)$_2$·2H$_2$O (0.27 g, 1 mmol) instead of Co(CH$_3$COO)$_2$·4H$_2$O. Complex **2** is a stable orange precipitate. The orange precipitate was dissolved in a hot DMF solution and was allowed to stand ca. 7 days at room temperature in the dark, affording the orange needle crystals suitable for X-ray crystallography. Yield: 75%. Anal. Calcd (%) for (C$_{16}$H$_{18}$N$_6$S$_2$-FeCd)$_2$·(C$_3$H$_7$NO)$_4$: C, 39.3; H, 4.8; N, 16.6. Found: C, 39.3; H, 4.7; N, 16.5. IR (KBr, cm^{-1}): 3481, 3289 (ν_{N-H}, ν_{O-H}, m), 1676 ($\nu_{C=N}$, s), 1496 (ν_{C-N}, s), 1296 (ν_{N-N}, m), 1039 ($\nu_{C=S}$, m).

Cu$_4$Fe$_2$ (3) [Cu(MeCN)$_4$]ClO$_4$ (0.114 g, 0.35 mmol) was added to a degassed solution of H$_2$L (0.073 g, 0.175 mmol) and Et$_3$N (25 μL, 0.175 mmol) in DMF (3 mL). The solution was layered with Et$_2$O, and after 24 h dark-red crystals of **3** were obtained. Anal. Calcd (%) for (C$_{16}$H$_{18}$N$_6$S$_2$FeCu$_2$)$_4$·(C$_3$H$_7$NO)$_2$(CH$_3$OH)$_{1.5}$: C, 36.4; H, 3.9; N, 15.4. Found: C, 36.9; H, 4.1; N, 15.5. IR (KBr, cm^{-1}): 3474, 3188 (ν_{N-H}, ν_{O-H}, m), 1588 ($\nu_{C=N}$, s), 1520 (ν_{C-N}, s), 1298 (ν_{N-N}, m), 1030 ($\nu_{C=S}$, m).

Crystallographic Analyses. Parameters for data collection and refinement of the three complexes are summiarized in Table 1.

Intensities of complexes **1**, **2**, and **3** were collected on a Siemens SMART-CCD diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.710\,73$ Å) using the SMART and SAINT programs.[19] Forty-five frames of data were collected at 298 K with an oscillation range of 1 deg/frame and an exposure time of 15 s/frame. Indexing and unit cell refinement were based on all observed reflections from those 45 frames. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL version 5.1.[20]All of the non-hydrogen atoms except the disordered solvent molecules were refined with anisotropic thermal displacement coefficients. Hydrogen atoms in the ferrocene−metal molecules were located geometrically, whereas those of solvent molecules were found on Fourier difference maps, and all the hydrogen atoms were refined in the riding model. The hydrogen atoms of the disordered water molecules in the structure **3** were not added and refined. Since the quality of the single crystal was not satisfactory, the observed/unique reflection ratio was only 37% and 31% for compounds **1** and **2**, respectively. The acetontrile and

(19) SMART and SAINT, Area Detector Control and Integration Software; Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1996.
(20) Sheldrick, G. M. *SHELXTL V5.1, Software Reference Manual*; Bruker, AXS, Inc.: Madison, WI, 1997.
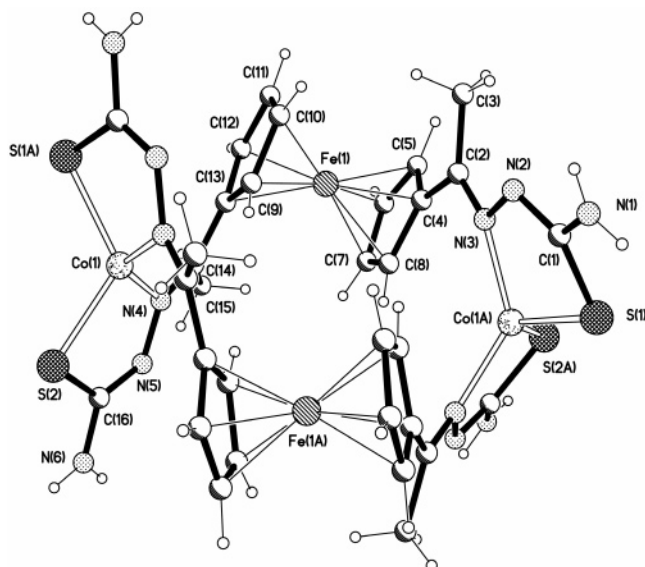
Figure 1. Molecular structure of complex **1** showing the atomic-numbering scheme, the solvent molecules are omitted for clarity. Symmetry code A: $-x, y, 1.5 - z$.

Table 2. Selected Distance (Å) and Angle (deg) for **1**[a]

Co(1)−N(4)	2.038(5)	N(2)−C(1)	1.274(6)
Co(1)−N(3A)	2.035(4)	N(2)−N(3)	1.408(6)
Co(1)−S(2)	2.247(2)	N(4)−N(5)	1.376(6)
Co(1)−S(1A)	2.250 (2)	N(5)−C(16)	1.308(9)
S(1)−C(1)	1.749(6)	N(6)−C(16)	1.336(8)
N(1)−C(1)	1.361(8)	S(2)−C(16)	1.743(6)
N(4)−Co(1)−N(3A)	133.8(2)	N(4)−Co(1)−S(1A)	118.6(1)
N(4)−Co(1)−S(2)	86.1(2)	N(3A)−Co(1)−S(1A)	86.2(1)
N(3A)−Co(1)−S(2)	116.4(2)	S(2)−Co(1)−S(1A)	119.5(1)

[a] Symmetry code A: $-x, y, 0.5 - z$.

water molecules in structure **1** were refined disordered. Since there are four slightly different ferrocene−metal molecules in an asymmetric unit of the structure **3**, more then 200 non-hydrogen atoms and more than 2000 parameters were refined on the basis of more than 25 000 reflections. It should be noted that such a refinement is almost beyond the upper limit of the SHELXTL program. The DMF molecules and methanol molecules in the structures were refined disordered with four DMF molecules occupying six disordered positions and three methanol molecules occupying four disordered positions. All the non-hydrogen atoms of the solvents molecules were refined isotropically. We do not try to find more atoms from the Fourier difference maps, since the largest peak is smaller than 1 and near to copper atoms. Also since there are four independent molecules in an asymmetric unit, the absolute configuration of the structure exhibits no meaning.

Measurements of SHG Response. The second-order nonlinear optical intensities are estimated by measuring the complex powder, whose diameters are from 76 to 154 μm in a pellet with a diameter as 10 mm. The thickness of each pellet is about 0.8 nm. The experimental arrangement for measuring the nonlinear optical properties utilizes an M200 high-power mode-locked Nd:YAG laser with 200 ps pulse at a repetition rate of 5 Hz. The selected wavelength is 1064 nm. According to the principle proposed by Kurtz and Perry, the SHG efficiency was estimated to be about 1.5 times that of KDP.

Results and Discussion

Crystal Structure of the Complex 1 Refluxing the methanol solution of $Co(CH_3COO)_2 \cdot 4H_2O$ and H_2L in the presence of KOH for 4 h gives the precipitate of compound **1** in good yield. As shown in Figure 1, compound **1** is a neutral double-helical molecule composed of two anionic ligands L^{2-} wrapped around two Co($^-$) ions that are separated by 7.51 Å like the Zn(II) analogy reported.[11e] The compound **1** possesses a crystallographic C_2 axis perpendicular to the helical Co···Co axis, with the four coplanar metal atoms forming a slightly distorted rhombus with sides of 4.90 Å and interior angles of 100° and 80°, respectively. Each Co-

(II) center occupies a four-coordinated pseudotetrahedral environment bound to two sulfur atoms and two imine nitrogen atoms from two different L^{2-} ligands with the dihedral angle between the two chelating planes being 82.6-(3)°. The Co−S distances (Table 2) of 2.248(2)−2.258(2) Å and Co−N distances of 2.036(5)−2.037(5) Å agree well with those in related compounds. The thiosemicarbazone moieties are twisted by ca. 50° from the Cp rings to which they are attached with dihedral angles between the two thiosemicarbazone moieties of 78.2°. Coordination to the metal center also forces twisting between the two side chains of one ferrocene moiety with a torsion angle C(2)−C(4)··· C(13)−C(14) of −122°. No significant deformation of the almost parallel Cp ring is observed. The measured C−S bond distances ca. 1.75 Å are within the normal range of a C−S single bond, indicating that the thiosemicarbazone moieties L^{2-} adopt the *thiol* tautomeric form in acting as a doubly charged negative ligand.[21] The C−N and N−N bond distances in L^{2-} are intermediate between formal single and double bonds, pointing to extensive electron delocalization over the entire molecular skeleton.[21]

The inherent chirality of the helical structure[22] and the metal ions displaying the same absolution configurations reveal that the helicand (helicand ligand) should be able to transmit the chirality from one metal center to another, and at the same time, the chirality of the first ligand decided that of the second one.[23] Detailed structural analysis reveals that chiral helices of the same configurations interact with each other through hydrogen bonds forming an infinite tube as shown in Figure 2. The imino nitrogen atoms of the thiosemicarbazone moieties act as H-bond acceptors while the amino nitrogen atoms act as donors, these pair up with the corresponding imino and amino nitrogen atoms of a parallel helix forming hydrogen bonds. The N···N separations are 3.18(1) and 3.16(1) Å for N(11)···N(15B) $(1 - x, 1 + y, 1 - z)$ and N(16)···N(12C) $(1 - x, 1 + y, 1 - z)$,

(21) (a) Ainscough, E. W.; Brodie, A. M.; Ranford, J. D.; Waters, J. M. *J. Chem. Soc.*, *Dalton Trans.* **1991**, 1737. (b) Katti, K. V.; Singh, P. R.; Barnes, C. L. *J. Chem. Soc., Dalton Trans.* **1993**, 2153. (c) Duan, C. Y.; Wu, B. M.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1996**, 3485.

(22) (a) Constable, E. C. *Polynuclear Transition Metal Helicates in Comprehensive Supramolecular Chemistry*; Sauvage, J. P., Ed.; Elsevier: Oxford, 1996; Vol. 9, pp 213−252. (b) Piguet, C.; Bernardinelli G.; Hopfgartner, G. *Chem. Rev.* **1997**, 97, 2005.

(23) (a) Hannon, M. J.; Bunce, S.; Clarke, A. J.; Alcock, N. W. *Angew. Chem., Int. Ed.* **1999**, 38, 1277. (b) Hamblin, J.; Jackson, A.; Alcock, N. W.; Hannon, M. J. *J. Chem. Soc., Dalton Trans.* **2002**, 1635. (c) (a) Guo, D.; Duan, C. Y.; Fang, C. J.; Meng, Q. J. *New. J. Chem.* **2002**, 26, 796.

(a)

(b)
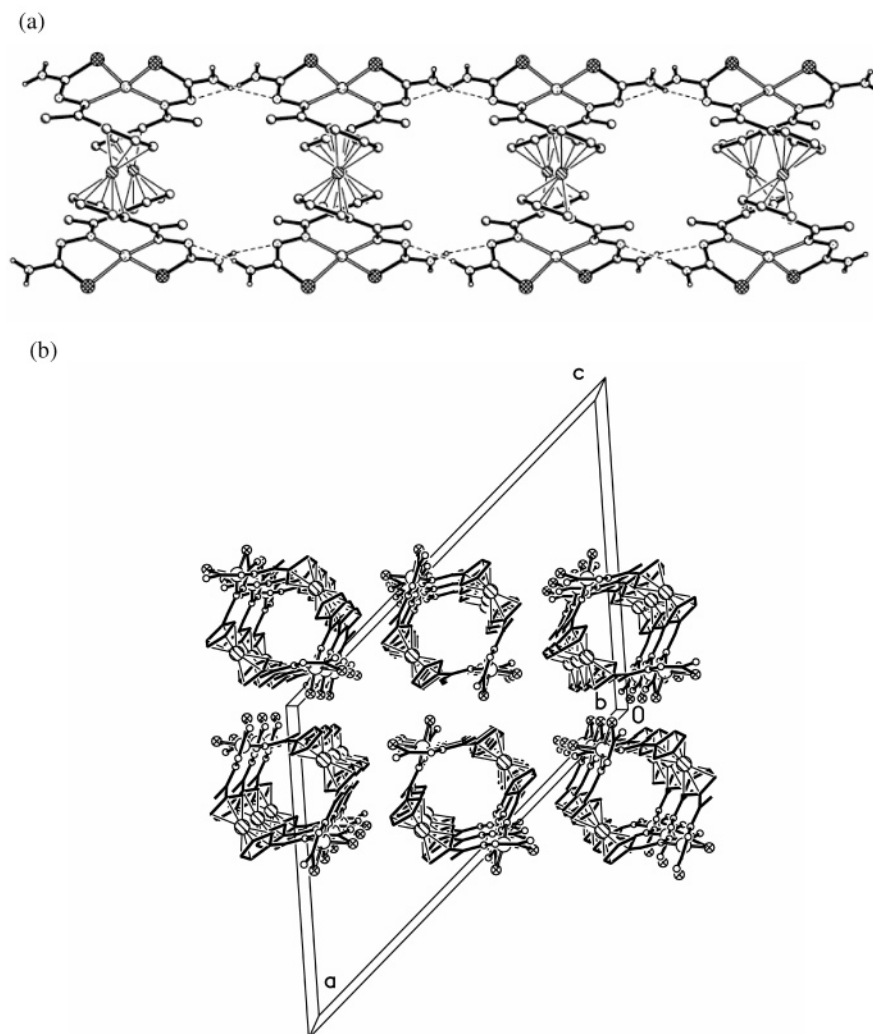
Figure 2. (a) View of the chiral hydrogen-bonding one-dimensional tube of **1**. (b) Packing diagram along the *b* axis showing the alignment of chiral chain with different chiralities.

respectively, while N−H···N angles are 156(1)° and 171° for N(11)−H(11B)···N(15B) and N(16)−H(16A)···N(12C), respectively. Since only the helicates with the same chiralities can be connected into one infinite chain, and the ferrocene-based ligands in one helicates exhibit the same chiralities, it is obligatory that all the cobalt ions in one infinite chiral chain have the same chiralities. Therefore, one may say that the chirality of the cobalt(II) is transmitted via the discriminative helical linkage or, alternatively, that the chirality of the chain is transmitted via the discriminative bridged units.[24] However, the chiral chains with opposite handness are aligned alternatively, so the whole crystal is heterochiral and hence racemic. The one-dimensional tube contains alternate cavities and walls (the double-helix molecules) reminiscent of a train. Each 'coach' includes two hydrogen bond dimeric water molecules with an O···O separation of ca. 2.93 Å. The O···O vector occupies a C_2 axis perpendicular to the helical

Co···Co axis. No obvious hydrogen bonds are seen between the guest molecules and the host.

The ferrocene-bridged double-helical complex and its novel hydrogen-bond supramolecular "trainlike" system are interesting. The unusual chiral recognition provides an opportunity to spontaneously resolve chiral species, which is very important in metallo-supramolecular chemistry.[25] This self-assembled nanostructure with host−guest interactions shows potential for broadening the scope for further work in self-assembly.

Crystal Structure of Complex 2 Refluxing the methanol solution of $Cd(CH_3COO)_2 \cdot 2H_2O$ and H_2L in the presence of KOH for 4 h give the precipitate of compound **2** in good yield. Orange needle crystals of complex **2** suitable for X-ray diffraction determination were grown by slow evaporation of its DMF solution at room temperature in the dark. Usually, the Cd(II) has the same d-electronic structures and similar

(24) (a) Gao, E. Q.; Yue, Y. F.; Bai, S. Q.; He, Z.; Yan, C. H. *J. Am. Chem. Soc.* **2004**, *126*, 1419. (b) Gao, E. Q.; Bai, S. Q.; Wang, Z. M.; Yan, C. H. *J. Am. Chem. Soc.* **2003**, *125*, 4984. (c) Orita, A.; Nakano, T.; An, D. L.; Tanikawa, K.; Wakamatsu, K.; Otera, J. *J. Am. Chem. Soc.* **2004**, *126*, 10389. (d) Provent, C.; Rivara-Minten, E.; Hewage, S.; Brunner, G.; Williams, A. F. *Chem. Eur. J.* **1999**, *5*, 3487.

(25) (a) Peŕez-Garcýa, L.; Amabilino, D. B. *Chem. Soc. Rev.* **2002**, *31*, 342. (b) Katsuki, I.; Motoda, Y.; Sunatsuki, Y.; Matsumoto, N.; Nakashima, T.; Kojima, M. *J. Am. Chem. Soc.* **2002**, *124*, 629. (c) Ezuhara, T.; Endo, K.; Aoyama, Y. *J. Am. Chem. Soc.* **1999**, *121*, 3279. (d) Tabellion, F. M.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1529.
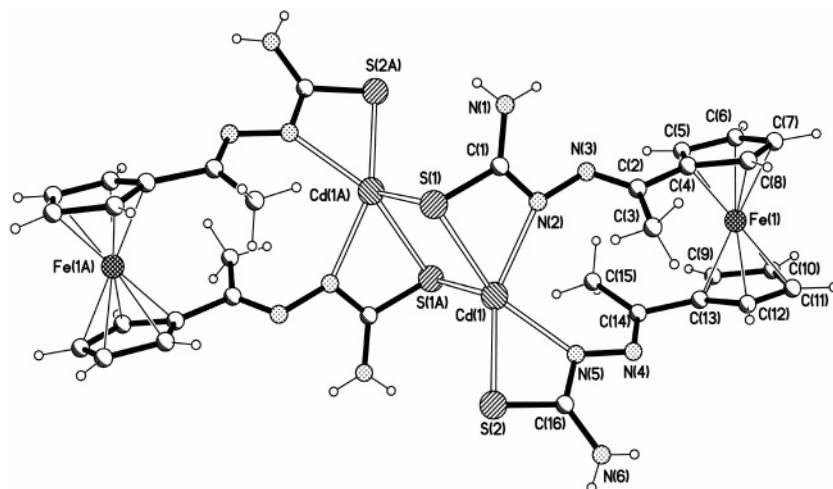
Figure 3. Molecular structure of complex **2** showing the atomic numbering scheme; the solvent molecules are omitted for clarity. Symmetry code A: 1 − x, 1 − y, −1 − z.

Table 3. Selected Distance (Å) and Angle (deg) for **2**[a]

Cd(1)−N(5)	2.281(8)	N(1)−C(1)	1.299(8)
Cd(1)−N(2)	2.283(6)	N(2)−C(1)	1.302(9)
Cd(1)−S(2)	2.536(3)	N(2)−N(3)	1.453(9)
Cd(1)−S(1)	2.776(2)	N(4)−N(5)	1.357(10)
Cd(1)−S(1A)	2.559(3)	N(5)−C(16)	1.358(12)
S(1)−C(1)	1.787(7)	N(6)−C(16)	1.301(11)
S(2)−C(16)	1.741(10)		
N(5)−Cd(1)−N(2)	99.6(2)	N(2)−Cd(1)−S(1)	60.4(2)
N(5)−Cd(1)−S(2)	64.3(2)	S(2)−Cd(1)−S(1)	115.1(1)
N(2)−Cd(1)−S(2)	139.3(2)	S(1)−Cd(1)−S(1A)	91.6(1)
N(5)−Cd(1)−S(1A)	116.9(2)	S(2)−Cd(1)−S(1A)	115.1(2)
N(2)−Cd(1)−S(1A)	104.3(2)	N(5)−Cd(1)−S(1)	149.2(2)

[a] Symmetry code A: 1− x, 1 − y, −1 − z.

coordination geometry to that of the Zn(II) analogy; however, the crystal structure of complex **2** shows the difference of both the coordination geometry and molecular structure from the zinc(II) and cadmium(II) complexes with the same ligand in the same reaction conditions. As shown in Figure 3, the complex **2** is a dimeric structure with two monocadmium-(II) units bridged by the sulfur atoms of the ligand. The coordination geometry about the Cd(II) atom is (4 + 1) distorted square-pyramidal with three Cd−S and two Cd−N bonds. The two sulfur atoms and the two imine nitrogen from one ligand constitute the basal plane with the fifth position occupied by a bridging sulfur from the other ligand to form the dimeric structure. The basal plane shows appreciable tetrahedral distortion (mean deviation from the best plane >0.2 Å), which deforms the square-pyramidal coordination polyhedron toward trigonal-bipyramidal geometry, as described by structural parameters according to the models of Gillespie[26] and Muetterties and Guggenberger.[27] It is interesting to compare the structure of the ligand in the free state and in the complex **2**. The largest difference may be due to the distance around atom C(1) (Table 3). In the free ligand,[11e] the bond distances of C(1)−N(2) of 1.35 Å and C(1)−S(1) of 1.69 Å suggest that C(1)−N(2) is the single bond and C(1)−S(1) is the double bond, while in the complex, the

(26) Gillespic, R. J. *J. Phys. Soc.* **1963**, 47672.
(27) Muetterties, E. L.; Guggenberger, L. T. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

bond distances of C(1)−N(2) of 1.28 Å and C(1)−S(1) of 1.78 Å show that C(1)−N(2) is the double bond and C(1)−S(1) is the single bond. These results indicate the presence of the Cd−S−Cd, formed by the elongation of the −NH−C≡S group in the free ligand to −N≡C−S−, and the ligand coordinates to the metal through the sulfur after deprotonation.

Since the thiosemicarbazone moieties have both the hydrogen bond donors (and/or acceptors), the dimeric species provide the possibility to form hydrogen bonds with the DMF molecules in the crystal. As shown in Figure 4, the oxygen atoms in the DMF molecules each interact with two hydrogen atoms from the amino groups of different molecules to form the one-dimensional hydrogen bonding chain. The separations for N(1)···O(1) and N(1)···O(2A) (symmetry code A: 1 + x, −1 + y, z) are 2.977(9) and 2.876(8) Å with the N−H···O angle being 168.1(3)° and 147.7(4)°, respectively. The separations for N(6)···O(1B) and N(6)···O(2) (symmetry code B: −1 + x, 1 + y, z) are 3.172(9) and 3.096(8) Å with the N−H···O angle being 139.4(3)° and 145.5(4)°, respectively. Since the dimeric structure has centric symmetry, the molecular structure and the infinite chain have no chirality at all.

Crystal Structure of Complex 3 In contrast to complexes **1** and **2** reported here, complex **3** is isolated from reaction of H_2L with [Cu(MeCN)$_4$]ClO$_4$ in DMF in the presence of triethylamine. X-ray single-crystal structure analysis reveals that there are four slightly different molecules in an asymmetric unit (Table 4). Figure 5 shows the molecular structure of one of the four molecules. The structure consists of four copper atoms and two ferrocene-based bisthiosemicarbazone clips. Each copper(I) is coordinated by one SN didentate chelating thiosemicarbazone moiety of one ligand and one sulfur atom from the other ligand. Each ligand coordinates to four copper(I) centers: two with the two thiosemicarbazone chelating moieties and two with the thiolate sulfur bridging atoms. The four metal atoms and the four bridging sulfur atoms form a crown-like Cu_4S_4 octagon similar to that of S_8 with two ferrocene-containing ligands positioned outside. The two ferrocene moieties are almost perpendicular
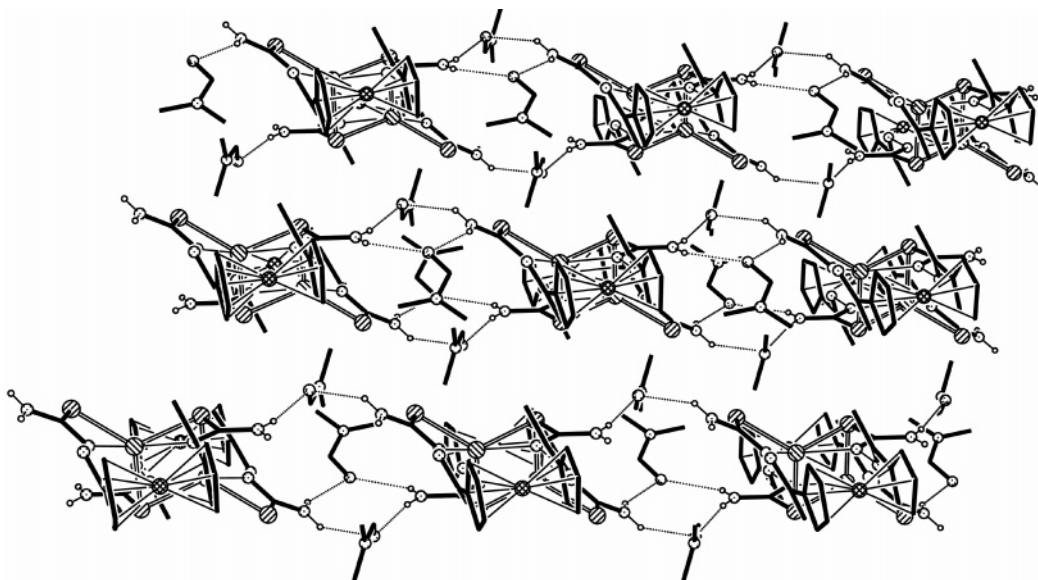
Figure 4. View of the crystal packing of compound **2** showing the hydrogen-bonding one-dimensional chain.
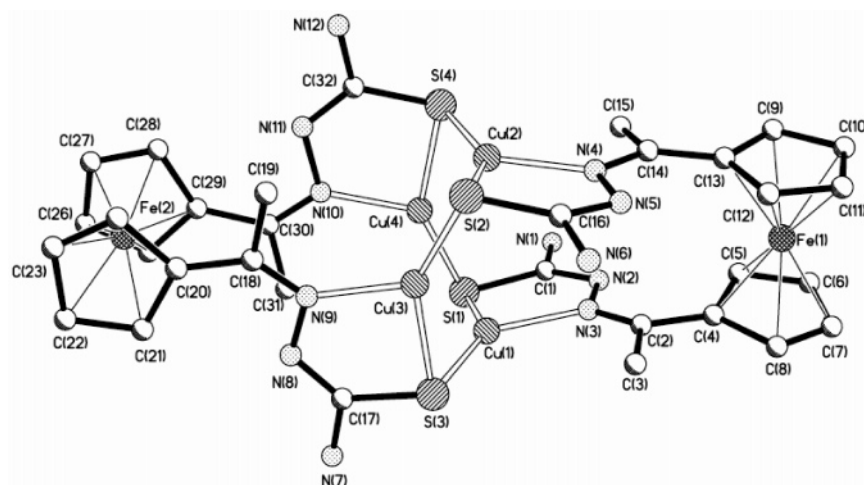

Figure 5. Molecular structure of **3** showing the atomic numbering scheme. Hydrogen atoms and the solvent molecules are omitted for clarity.

Table 4. Selected Distance (Å) and Angle (deg) for **3**

Cu (1)−N(3)	2.067(5)	S(4)−C(32)	1.768(8)
Cu(1)−S(3)	2.188(3)	N(1)−C(1)	1.381(8)
Cu(1)−S(1)	2.232(3)	N(2)−C(1)	1.277(8)
Cu(2)−N(4)	2.026(5)	N(2)−N(3)	1.360(7)
Cu(2)−S(4)	2.167(3)	N(4)−N(5)	1.395(8)
Cu(2)−S(2)	2.232(3)	N(5)−C(16)	1.355(9)
Cu(3)−N(9)	2.042(5)	N(6)−C(16)	1.379(9)
Cu(3)−S(2)	2.179(3)	N(7)−C(17)	1.358(8)
Cu(3)−S(3)	2.228(3)	N(8)−C(17)	1.323(9)
Cu(4)−N(10)	2.019(5)	N(8)−N(9)	1.365(7)
Cu(4)−S(1)	2.219(3)	N(10)−N(11)	1.402(8)
Cu(4)−S(4)	2.224(3)	N(11)−C(32)	1.294(9)
S(1)−C(1)	1.768(7)	N(12)−C(32)	1.316(9)
S(2)−C(16)	1.636(9)	S(3)−C(17)	1.766(7)
N(3)−Cu(1)−S(3)	133.3(2)	N(9)−Cu(3)−S(3)	88.0(2)
N(3)−Cu(1)−S(1)	86.8(2)	S(2)−Cu(3)−S(3)	143.1(1)
S(3)−Cu(1)−S(1)	138.0(1)	N(9)−Cu(3)−S(2)	127.2(2)
N(4)−Cu(2)−S(4)	127.3(4)	N(10)−Cu(4)−S(1)	127.3(2)
N(4)−Cu(2)−S(2)	86.8(2)	N(10)−Cu(4)−S(4)	87.9(2)
S(4)−Cu(2)−S(2)	143.8(1)	S(1)−Cu(4)−S(4)	143.5(1)

to each other, with the dihedral angles of the Cp rings in different ligands being 83° on average. Such a special arrangement of the two ferrocene-based ligands leads to the presence of chirality of the hexanuclear Cu_4Fe_2 complex. And detailed structural analyses indicate that the four molecules in an asymmetric unit are two pairs of racemates. The deprotonation of the ligand on coordination is also evident in the observed bond lengths in the cluster. The C−S bond distance increases from 1.69 Å in the H_2L to 1.75 Å in **3**, and there is also a decrease in length of the C(1)−N(2) bond from 1.35 to 1.29 Å, indicating that the −N=C−S− thiolate resonance predominates in the complex. Since the compound **3** crystallizes in the chiral space group $P2_1$, it prompts an investigation of optical activity. Preliminary investigation shows that the compound **3** is SHG active with the SHG response about 1.5 times that of KDP. The chiral conformation of the molecule is essential for second-order optical nonlinearity.[28]

Redox Properties of Compounds 1−3. The differential pulse voltammetry (DPV) technique is employed to obtain well-resolved potential information, while the individual redox processes for the multinuclear complexes are poorly resolved in the CV experiment, in which individual $E_{1/2}$
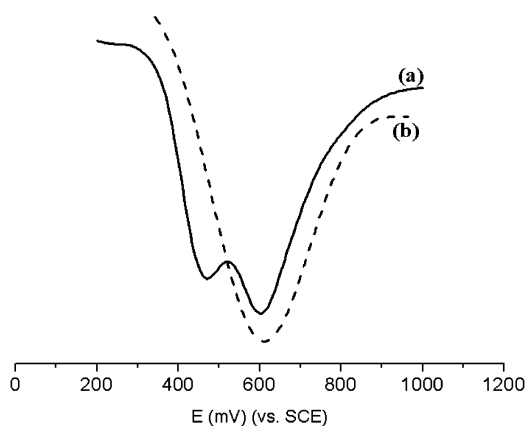
Figure 6. Differential pulse voltammogram of the complexes **1** (a) and **2** (b) in DMF solution containing n-Bu$_4$NClO$_4$ (0.1 M) at a scanning rate of 20 mV s^{-1} (vs SCE).

potentials cannot be easily or accurately exacted from the data.[29] While the differential pulse voltammetry of compound **1** shows two successive redox peaks with half-wave potentials ($E_{1/2}$) at 449 and 604 mV, corresponding to the two single-electron oxidations of the ferrocene moieties, the compound **2** exhibits only one redox peak at 627 mV, respectively (Figure 6). Such results reveal the presence of ferrocene–ferrocene interactions in compound **1**.

In general, the molecules containing metallocenyl units could accommodate a particular metal ion at its coordination site and undergo a concurrent redox change. And polyferrocenes generally undergo reversible one-electron oxidations, with the number of waves being determined by the number of ferrocenyl units.[30] The half-wave potentials of the redox processes and the separation (ΔE) between consecutive waves vary over a wide range, depending on the nature of the compounds.[31] Although the bridged metal moieties can accommodate a range of coordination geometry, it is likely

that only negligible structural changes accompany one-electron oxidation of these complexes, since crystallographic data on ferrocene[32] and its salts[33] indicate that the oxidation state and charge of the iron atom have almost no effect on the interatomic distances. Considering that the intramolecular iron–iron separation of 6.34 Å for compound **1** is smaller than 7.6 Å, the average encounter diameter between the ferrocene and ferricenium ion in solution, and that the intramolecular iron–iron separation of 14.5 Å for complex **2** is much larger than 7.6 Å, the different electrochemistries of the complexes **1** and **2** should contribute to the through-space metal–metal Coulomb contribution.

DPV of the compound **3** shows two successive oxide peaks with half-wave potential ($E_{1/2}$) at 350 and 725 mV, assigned to the oxidations of the Cu(I) moieties and ferrocene moieties, respectively. The broad shape of the first redox peaks might be caused by the overlap of the irreversible oxidation of the four copper centers containing sulfur. Since the intramolecular iron–iron separation of 12.5 Å is also much larger than the average encounter diameter between the ferrocene and ferrocenium ion in solution, it is suggested the Cu$_4$S$_4$ cluster is not a good molecular wire for the electronic coupling between the two ferrocene moieties.

Summary

In summary, this paper describes the construction of three discrete heterodimetallic compounds, Co$_2$Fe$_2$, Cd$_2$Fe$_2$ and Cu$_4$Fe$_2$, from a ferrocene-based thiosemicarbazone clips. It is suggested that the coordination geometry of the metal centers can influence the coordination mode of the thiosemicarbazone moieties and then the molecular structures they formed. Electrochemical measurements suggest that the complex **1** can effectively transmit the redox effects of the ferrocene moieties, while complex **2** and **3** cannot.

Supporting Information Available: Tables of detailed crystallographic data, atomic positional parameters, anisotropic displacement parameters, and bond length and angles in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) (a) Zyss, J. *Molecular Nonlinear Optics, Materials, Physics, and Devices*; Academic Press: New York, 1993. (b) Newnham, *Structure–Property Relations*; Springer: New York, 1975. (c) Xiong, R. G.; Xue, X.; Zhao, H.; You, X. Z.; Abrahams, B. F.; Xue, Z. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 3800.
(29) (a) Serr, B. R.; Andersen, K. A.; Elliott, C. M.; Anderson, O. P. *Inorg. Chem.* **1988**, *27*, 4499. (b) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.
(30) Beer, P. D. *Adv. Inorg. Chem.* **1992**, *39*, 79.
(31) (a) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086. (b) Callahan, R. W.; Keene, F. R.; Mayer, T. J.; Salmon, D. J. *J. Am. Chem. Soc.* **1974**, *96*, 7827. (c) Weaver, T. R.; Mayer, T. J.; Adeylmi, S. A.; Brown, G. M.; Eckberg, R. P.; Hatfield, E.; Johnson, E. C.; Murray, R. W.; Unterker, D. *J. Am. Chem. Soc.* **1975**, *97*, 3039. (d) Morrison, W. H., Jr.; Krogsrud, S.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 1998.

(32) Rosenblum, M. *Chemistry of the Iron Group Metallocenes*; New York, **1965**.
(33) Berstern, T.; Herbstein, F. H. *Acta Crystallogr. Sect B* **1968**, *24*, 1546.